

*Final Report*

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**Multi-Color Electrochromic Polymer Coatings**

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13. ABSTRACT (Maximum 200 Words) We have developed new routes to prepare a series of derivatized electron-rich carbazole polymers containing polar ion transport, solubilizing, and redox active pendant substituents providing both multiple redox and multiple color states for electrochromic coatings. A series of electroactive (electrochromic and electroluminescent) conjugated polyelectrolytes based on 1,4-phenylene and 2,5-thienylenen linkages and containing both sulfonate and ammonium ion derivatized have been prepared. These polymers have been used in layer-by-layer electrostatic deposition processes for the preparation of electrochromic coatings, along with LED's.					
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## **1. Objectives**

This research involved the design and preparation of a family of multi-color electrochromic polymers which can be used in electrochromic coatings applications on flexible, curved and irregular surfaces. These materials are especially directed to applications in chameleon surfaces. At the same time, numerous other applications potentially exist for these materials, including dialed-tint windows, electrochromic displays, thermal control, and in some instances, microwave and IR signature reduction.

## **2. Status of Effort**

We have developed our new routes to prepare a series of derivatized electron-rich carbazole polymers containing polar ion transport, solubilizing, and redox active pendant substituents providing both multiple redox and multiple color states for electrochromic coatings. A series of electroactive (electrochromic and electroluminescent) conjugated polyelectrolytes based on 1,4-phenylene and 2,5-thienylene linkages and containing both sulfonate and ammonium ion derivatized have been prepared. These polymers have been used in layer-by-layer electrostatic deposition processes for the preparation of electrochromic coatings, along with LED's.

## **3. Accomplishments**

### **3.1 Multi Color Electrochromic Carbazole Based Polymers**

We have synthesized a series of new electrochromic polymers for use in multi-color electrochromic coatings. We have developed a series of 3,6-bis(2-EDOT)carbazole (BEDOT-Cz) polymers as low-oxidation potential, three color electrochromic materials. These materials show three distinct color states as shown in Figure 1 below. In its reduced form the polymer is pale yellow, in its partially oxidized (radical cation) form it is green, and when it is fully oxidized (dication), it is blue. This multichromism makes the PBEDOT-Czs good candidates for use in multi-colored coatings required in chameleon-type applications.

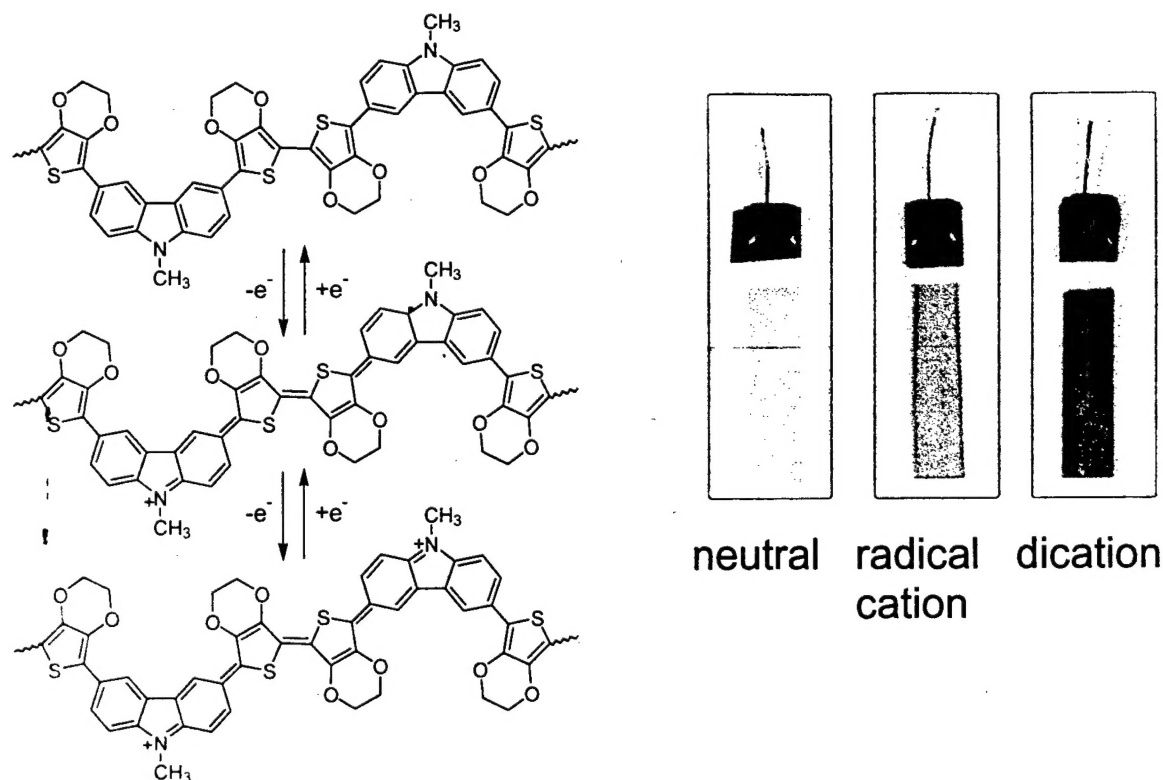
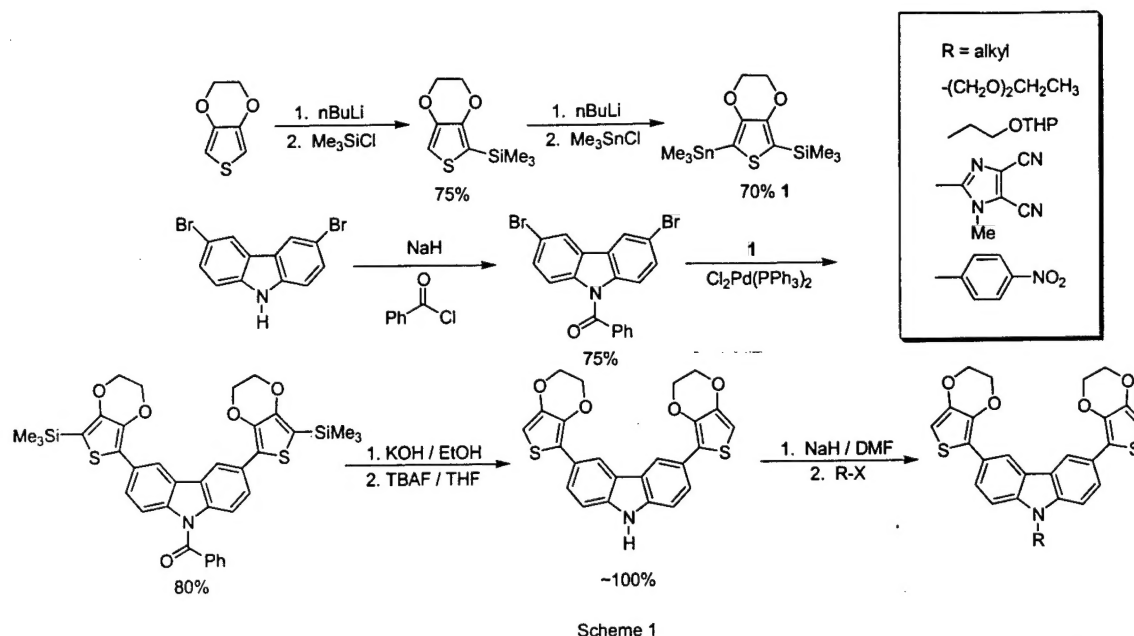


Figure 1

As reported previously, we have successfully developed the first synthetic route to unsubstituted BEDOT-Cz. This allows for the easy functionalization of the BEDOT-Cz core with a broad variety of substituents. Scheme 1 shows the synthesis of the unsubstituted derivatives and the functionalized derivatives. We have especially been interested in appending electron withdrawing groups on the carbazole unit in hopes of raising the band gap of the polymer. If the band gap can be raised to above 2.8 eV, then a polymer with a very transmissive reduced form will be obtained. The dicyanoimidazole and nitro benzene substituents shown in Scheme 1 were synthesized to this effect. Unfortunately, while the monomer derivatization proceeded cleanly, the monomers could not be electropolymerized. This may be due to the strong electron withdrawing nature of these substituents or possibly to charge transfer complex formation.

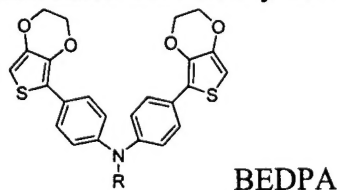


A second method attempted to raise the band gap was to change the heterocycle from EDOT to thiophene. Polythiophene has a band-gap that is 0.8 eV higher than PEDOT, so its incorporation should raise the gap. 3,6-bis(2-thienyl)carbazole (BThCz) was synthesized in much the same way as the BEDOT-Cz as in Scheme 1 (structure shown below).



Although it polymerized to an electroactive polymer, the band gap was almost unchanged, showing again the same three colors. It should be noted that the thiophene version exhibited very slow response times (up to 20 s to oxidize), proving the usefulness of EDOT in these systems.

One final attempt at raising the band-gap of these systems was to make a system with more conformational flexibility in the backbone. Along these lines, bis(EDOT)-diphenylamine (BEDPA) was synthesized in a similar manner as the previous derivatives using Stille coupling chemistry (structure shown below). Again, this monomer polymerized well to an electroactive polymer, but the band-gap was not increased but actually decreased to 2.2 eV.



In summary, a new synthetic route to unsubstituted BEDOT-Cz was developed so that many different functionalized monomers can be synthesized from one molecule. Alkyl and glyme substituted derivatives electropolymerize to highly electroactive multicolor polymers that switch rapidly from yellow to green to blue. Functionalization with electron withdrawing substituents and different heterocycles occurs cleanly, but unfortunately no band gap increases occurred.

### 3.2 Electrochromic Coatings Via Electrostatic Deposition

Layer-by layer deposition of polyelectrolytes via alternating electrostatic deposition of oppositely charged polymers provides a uniquely new coating method for the preparation of electrochromic coatings. A layer is deposited by dipping an appropriate substrate into an aqueous solution of polyelectrolyte. Alternating dips between cationic and anionic solutions allows multiple layer deposition and film formation. This process allows for more uniform layers to be formed than with electropolymerization, where small defects in the original conducting surface lead to inhomogenous films. Useful optical and redox properties may be achieved considering the alternating layer device makeup is only limited by the availability of such soluble, electroactive polymers.

Our original work focused on the synthesis and optical properties of poly[2,5-bis(2- $\{N,N,N$ -triethylammonium} ethoxy)-1,4-phenylene-*alt*-1,4 phenylene] dibromide (**PPP-NEt<sub>3</sub><sup>+</sup>**). [Scheme 2] This blue luminescent polymer can be electrostatically deposited onto conductive substrates such as indium tin oxide (ITO) coated glass. The synthesis has been enhanced using a more active palladium catalyst [PdCl<sub>2</sub>(dppf)] resulting in a polymer with high molecular weight ( $M_w = 22100 \text{ g mol}^{-1}$ ), low polydispersity (PDI = 1.18), and high yield (95%). [Table 1]. The polymer has been used in electrostatic dipping to create blue LED devices (via collaboration with Michael Rubner/MIT) and as the buffer layer in the creation of hybrid ink-jet printed LED devices (via collaboration with Yang Yang/UCLA).

Scheme 2. Polymerization route for **PPP-NEt<sub>3</sub><sup>+</sup>**.

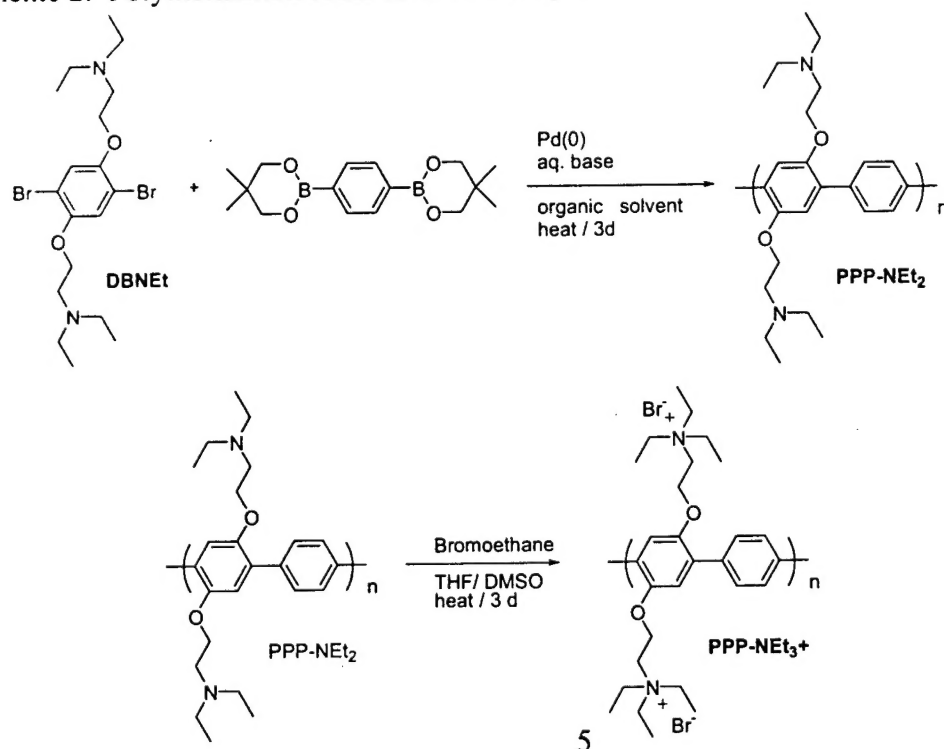


Table 1. GPC molecular weight data for **PPP-NEt<sub>2</sub>** in CHCl<sub>3</sub>.

catalyst	reaction solvent	yield	calibration method	$\overline{M}_n$ kg mol <sup>-1</sup>	$MP$ kg mol <sup>-1</sup>	$\overline{M}_w$ kg mol <sup>-1</sup>	$\overline{M}_w/\overline{M}_n$
<b>Pd(OAc)<sub>2</sub></b>	THF	38%	PS	5.0	4.8	19.5	3.91
			PPPa	3.9	3.8	12.9	3.29
<b>Pd(OAc)<sub>2</sub></b>	DMF	76%	PS	15.9	24.3	35.0	2.20
			PPP	10.8	15.6	21.5	1.99
<b>PdCl<sub>2</sub>(dppf)</b>	THF	95%	PS	18.7	19.4	22.1	1.18
			PPP	12.4	12.8	14.4	1.16
<b>Pd(OAc)<sub>2</sub></b>	acetone	92%	PS	12.6	21.4	28.6	2.27
			PPP	8.8	14.0	18.0	2.05

<sup>a</sup>Universal calibration using values derived for PPP in THF.

Subsequently, we have focused on the synthesis of the green emitting polymer poly{2,5-bis[2-(*N,N,N*-triethylammonium)-1-oxapropyl]-1,4-phenylene-*alt*-2,5-thienylene} dibromide (**PPT-NEt<sub>3</sub><sup>+</sup>**). By incorporation of the more electron rich thiophene unit into the back bone of the polymer, the absorbance maximum ( $\lambda_{\max} = 411$  nm) is red shifted compared to the **PPP-NEt<sub>3</sub><sup>+</sup>** with a corresponding emission  $\lambda_{\max} = 494$  nm for the **PPT-NEt<sub>3</sub><sup>+</sup>** in pH = 7 water. Scheme 3 outlines the general polymerization route. The best molecular weights, [**PPT-NEt<sub>2</sub>(96-drop)**], were achieved with a Stille reaction with dropwise addition of 2,5-bis(trimethyltin)thiophene to the reaction solution containing solvent, DMF, catalyst, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and 2,5-bis(3-[*N,N*-diethylamino]-1-oxapropyl)-1,4-diiodobenzene (**DINet**). The neutral polymer intermediate is analyzed for molecular weight properties (along with complete characterization) and then subjected to treatment with bromoethane to quaternize the amine sites, thereby producing the desired water soluble polymer. Table 2 shows the molecular weight data obtained for various experimental conditions. Table 3 summarized the optical properties for both the neutral and water soluble forms of the PPP and PPT derivatives.

Scheme 3. Polymerization route for **PPT-NEt<sub>3</sub><sup>+</sup>**.

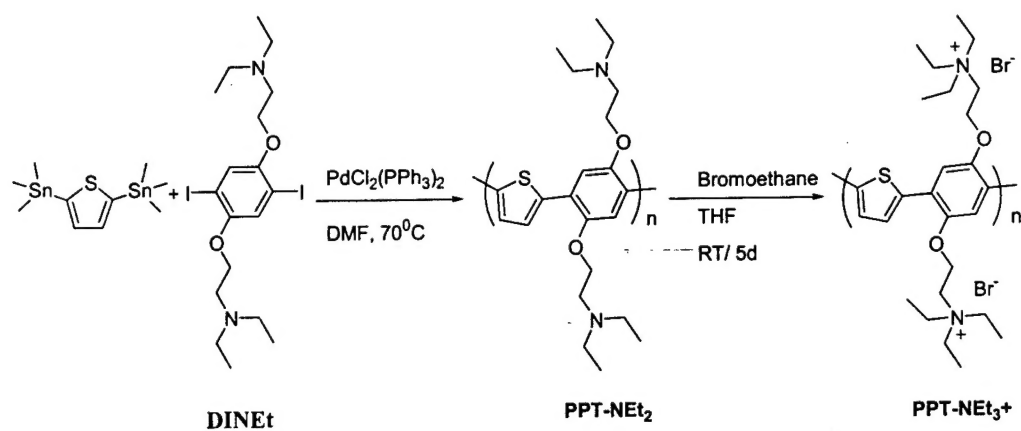


Table 2. GPC molecular weight data for **PPT-NEt<sub>2</sub>** in THF.

polymer	reaction solvent	reaction type	reaction time (hours)	$\overline{M}_n$ kg mol <sup>-1</sup>	$MP$ kg mol <sup>-1</sup>	$\overline{M}_w$ kg mol <sup>-1</sup>	$\overline{M}_w/\overline{M}_n$
<b>PPT-NEt<sub>2</sub></b> (48)	DMF	Stille	48	3.2	4.3	5.2	1.70
<b>PPT-NEt<sub>2</sub></b> (96)	DMF	Stille	96	4.1	5.8	6.9	1.68
<b>PPT-NEt<sub>2</sub></b> (240)	DMF	Stille	240	4.2	5.4	7.2	1.71
<b>PPT-NEt<sub>2</sub></b> (96-drop)	DMF	Stille (dropwise)	96	5.3	6.9	9.0	1.70

number in parenthesis indicates time of reaction

dropwise indicates thiophene reagent added to reaction slowly via an addition funnel



Table 3. Optical Property Summary for PPP-NEt and PPT-NEt polymers.

Polymer	Eg ( $\lambda_{\max}$ )	Film Color	Emission $\lambda_{\max}$ (nm)	Emission Color (Solution)
PPP-NEt <sub>2</sub>	3.3 eV (351 nm)	Tan	410	Blue
PPP-NEt <sub>3</sub> <sup>+</sup>	3.4 (330)	Tan	400	Blue
PPT-NEt <sub>2</sub>	2.4 (460)	Red	519	Green
PPT-NEt <sub>3</sub> <sup>+</sup>	2.6 (411)	Red	494	Green

A sulfonated poly(aniline) (PANI-SO<sub>3</sub>) polymer was used successfully in electrostatic depositions with a cationic non-electroactive poly(allyl amine hydrochloride) to produce a thin film device that showed electrochromism. These experiments represent the first time a conjugated polyelectrolyte has been used in layer-by-layer deposited electrochromic devices and may prove especially important in forming conformable coatings. Figure 2 shows that these polymers properly form multi-layers as evidenced by the linear increase of optical absorbance with the number of bilayers.

Spectroelectrochemistry was then used to probe the electrochromic properties of this film. As shown in Figure 3, by stepping the applied potential from 0.0 V to 0.55 V in increments, the film showed an increase in optical density in the visible region as desired.

Figure 2. PANI-SO<sub>3</sub>/PAH film build-up monitored by UV-Vis spectrophotometry.

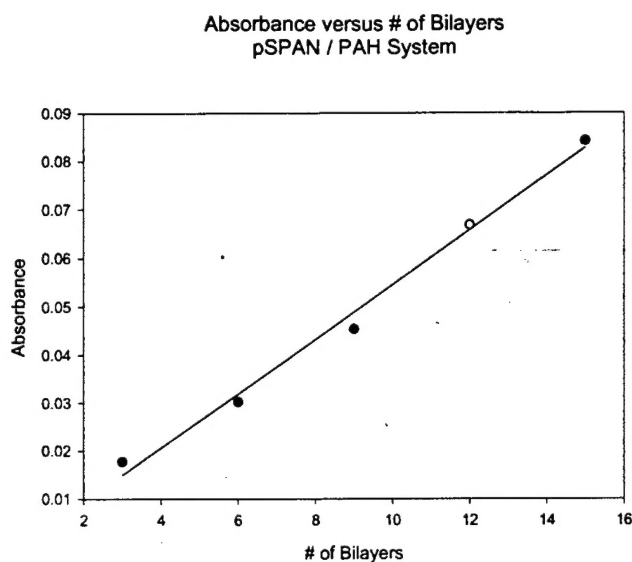
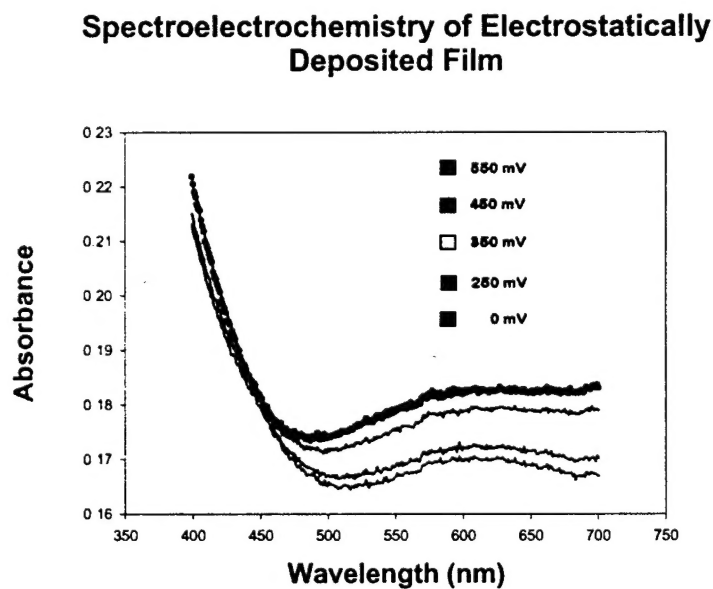


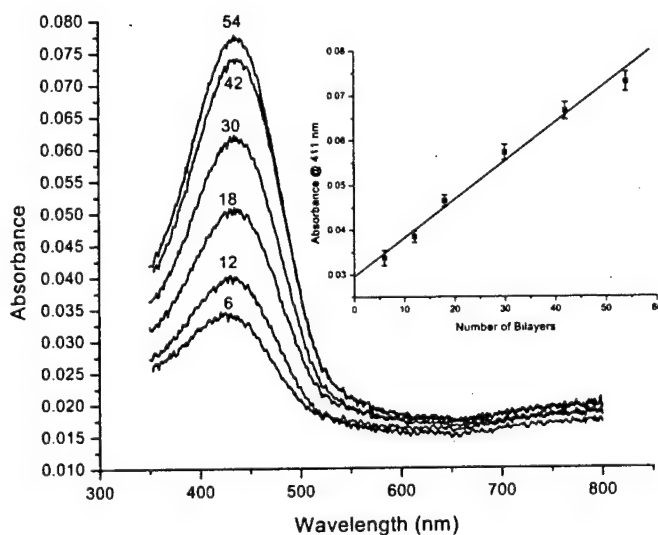
Figure 3. Spectroelectrochemical response from a PANI-SO<sub>3</sub>/PAH electrostatically deposited film.



In a similar manner to the above trial experiments, PPT-NEt<sub>3</sub><sup>+</sup> thin multi-layer films were constructed on hydrophilic ITO covered glass slides using the electrostatic deposition

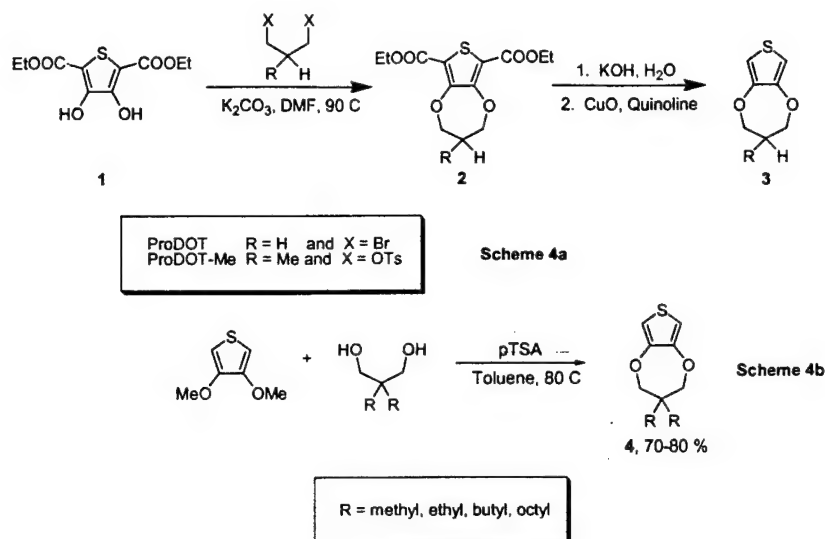
technique. ITO slides were alternately dipped in **PPT-NEt<sub>3</sub><sup>+</sup>** and poly(styrene sulfonic acid) sodium salt solutions ( $1 \times 10^{-3}$  M each, based on repeat unit molecular weight) for 3 minutes each with distilled water washing (3 minutes) between steps. Figure 4 shows a plot of the UV-Vis spectrum of the ITO slide as the number of deposited bilayers was increased from 6 to 54. The inset plot shows the absorbance at 411 nm versus the number of bilayers for the deposition. These absorbance values are given as the average value measured between 3 different ITO slides. A linear relationship is reflected ( $r = 0.99$ ), indicating that the deposition was a well-controlled process with approximately the same amount of polymer being deposited per dip after an initial conditioning of the surface for the first 5 bilayers. Photoluminescent experiments with excitation at 411 nm revealed a broad luminescence from the thin film centered around 550 nm. Subsequent attempts to achieve an electrochromic response from the films revealed only an irreversible oxidation wave for the PPT polymer.

Figure 4. UV-Vis spectra of PPT-NEt<sub>3</sub><sup>+</sup> electrostatically deposited films as number of bilayers increase from 6 to 54. Inset: Absorbance at 411 nm versus number of bilayers.



### 3.3 Soluble High Contrast Electrochromic Polymers Based on Poly(3,4-propylenedioxythiophene)s

We have developed a series of soluble electrochromic polymers based on poly(3,4-propylenedioxythiophene)s (PProDOTs). A series of these derivatives has been synthesized by a double Williamson etherification reaction, followed by ester hydrolysis and decarboxylation as depicted in Scheme 4a.



This route is fine for substrates that are not disubstituted on the middle carbon of the propylene bridge. To make the regio-symmetric disubstituted monomer 4, a different approach was necessary. Through the transesterification chemistry shown in Scheme 4b, disubstituted monomers have now been synthesized.

Electropolymerization on ITO coated glass slides of ProDOT-Me<sub>2</sub> yields polymers with very high contrast in the visible region ( up to 78%) and also very rapid response times (down to 0.2 s) for redox switching. Figure 5 below illustrates the color change between the reduced and oxidized forms of these films.

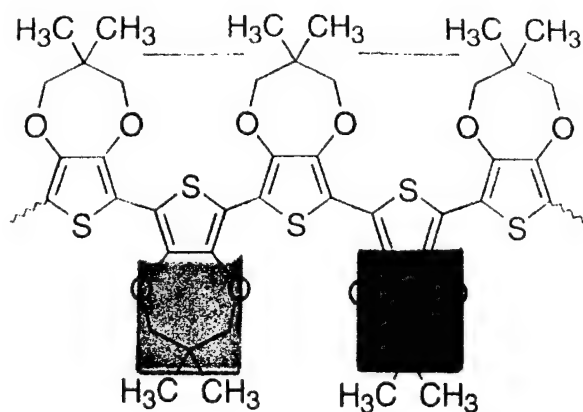
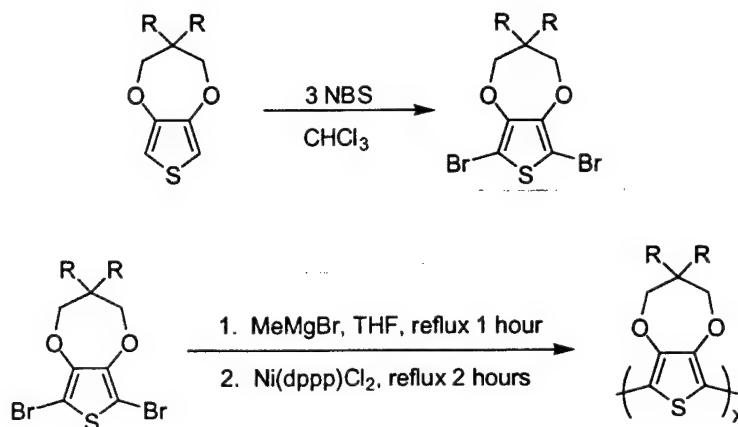


Figure 5

In order to be able to process these materials in typical manners, such as drop-casting and spin-coating, soluble polymers of these derivatives were made via the Grignard metathesis polymerization scheme. The polymerization route is depicted in Scheme 5; polymers have been synthesized where R= butyl and octyl. This method yields neutral polymers that can be

characterized by traditional methods such as NMR, GPC, and solution spectroscopy. Solutions of these films are red-violet in the reduced form and an almost colorless blue-tinged color in the oxidized form.



Solution doping experiments in dichloromethane with  $\text{SbCl}_5$  as the oxidant show the evolution of the band structure to be similar to that of the electropolymerized version, with very high contrast evident. Note that the conducting form is almost colorless. This data along with a picture of the two solutions are shown in Figure 6 below.

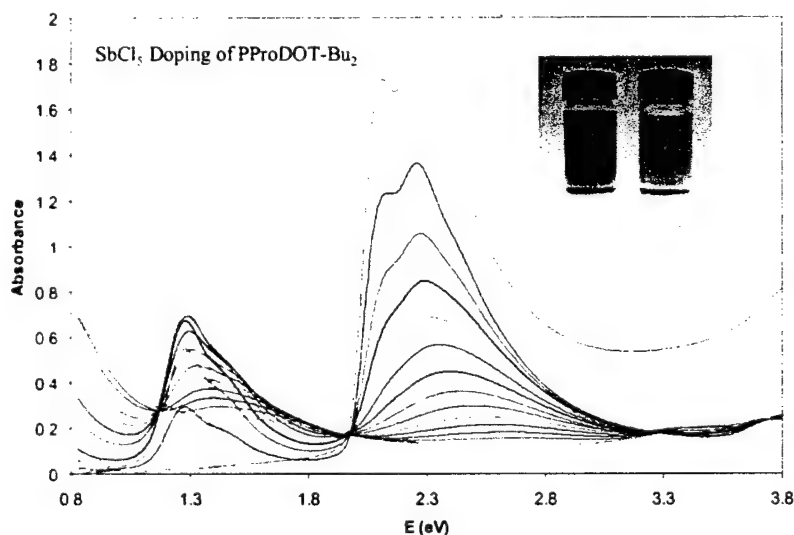


Figure 6

Because of the rigid-rod nature of conjugated polymers, GPC is a poor method to obtain accurate molecular weights. Along these lines, MALDI experiments have been initiated to obtain more absolute molecular weight values. MALDI experiments have shown that polymer chains are present from 10-50 rings. Figure 7 below shows a typical MALDI trace for PProDOT- $\text{Bu}_2$ .

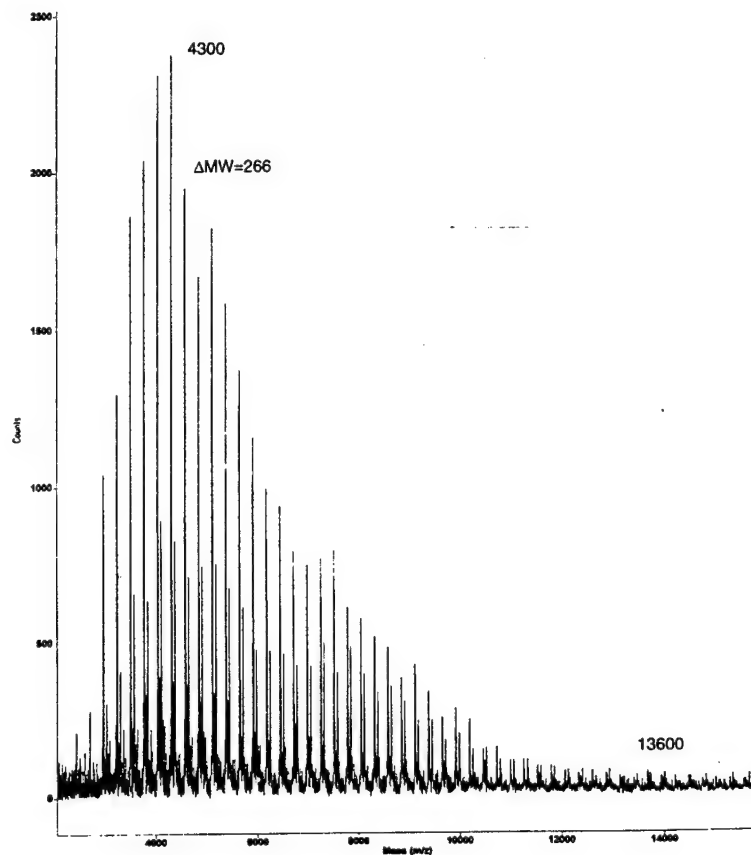


Figure 7

In summary, new soluble electrochromic polymers based on poly(3,4-propylenedioxythiophene)s have been synthesized by Grignard metathesis polymerization. These materials can be characterized by NMR, GPC, and MALDI. Solution doping studies with  $\text{SbCl}_5$  oxidant show that a very transmissive conducting polymer can be obtained at high doping levels.

## Personnel Supported

Mohamed Bouguettaya, Postdoctoral Fellow  
Alan Hopkins, Postdoctoral Fellow  
Michael Ramey, Graduate Student  
Jerry Reddinger, Graduate Student  
Greg Sotzing, Graduate Student  
Christopher Thomas, Graduate Student  
Dean Welsh, Graduate Student

John Reynolds, Principal Investigator

## Peer Reviewed Publications

Sotzing, G. A., Thomas, C. A., Reynolds, J. R., Steel, P. J.  
*Macromolecules*, **31**, 3750-3752 (1998).

"Low Band Gap, p- and n-Dopable Cyanovinylenes Polymers Containing Ethylenedioxythiophene"

Baur, J. W., Kim, S., Balanda, P. B., Reynolds, J. R., Rubner, M. F.  
*Adv. Mater.*, **10**, 1452-1455 (1998).

"Thin Film Light Emitting Devices Based on Sequentially Adsorbed Multilayers of Water Soluble Poly(p-phenylene)s".

Chang, S.-C., Bharathan, J., Helgeson, R., Wudl, F., Yang, Y., Ramey, M. B., Reynolds, J. R.  
*Appl. Phys. Lett.*, **73**, 2561-2563 (1998).

"Dual-Color Polymer Light-Emitting Pixels Processed by Hybrid Inkjet Printing"

Balanda, P. B., Ramey, M. B., Reynolds, J. R.  
*Macromolecules*, **32**, 3970-3978 (1999).

"Water Soluble and Blue Luminescent Cationic Polyelectrolytes Based on Poly(p-phenylene)"

Baur, J. W., Rubner, M. F., Reynolds, J. R., Kim, S.  
*Langmuir*, **15**, 6460-6469 (1999).

"Förster Energy Transfer Studies of Polyelectrolyte Heterostructures Containing Conjugated Polymers: A Means to Estimate Layer Interpenetration"

Wang, F., Wilson, M. S., Rauh, R. D., Schottland, P., Thompson, B. C., Reynolds, J. R.  
*Macromolecules*, **33**, 2083-2091 (2000).

"Electrochromic Linear and Star Branched Poly(3,4-Ethylenedioxythiophene-Didodecyloxybenzene) Polymers"

Groenendaal, L. B., Jonas, F., Freitag, D., Pielartzik, H., Reynolds, J. R.  
*Adv. Mater.*, **12**, 481-494 (2000).

"Poly(3,4-Ethylenedioxythiophene) and Its Derivatives: Past, Present and Future"

## Interactions and Transitions

### **Presentations and Conference Proceedings**

Air Force Kick-Off Workshop on Advanced Coatings Concepts, Wright-Patterson AFB, May 1997.

American Chemical Society, 214th National Meeting, Las Vegas, NV, September 1997.  
"Easily Functionalized 3,4-Ethylenedioxythiophenes" with D. M. Welsh and A. Kumar, *Polym. Preprints*, **38**(2), 320 (1997).

Materials Research Society, 1997 Fall Meeting, Boston, MA, December 1997.  
"Low Band Gap Conjugated Polymers as High Contrast Electrochromic Materials" with A. Kumar, M. Morvant, G. A. Sotzing, C. A. Thomas, and D. M. Welsh.

American Chemical Society, 215th National Meeting, Dallas, TX, March 1998.  
"Low Band Gap and n-Dopable Conjugated Polymers Based on 3,4-Ethylenedioxythiophene (EDOT)" with G. A. Sotzing, C. A. Thomas and D. J. Irvin, *Polym. Preprints*, **39**(1), 83 (1998).

American Chemical Society, 215th National Meeting, Dallas, TX, March 1998.  
"Low Band Gap and n-Dopable Cyanovinylene Based Polymers for Near IR Electrochromic Applications", with C. A. Thomas and G. A. Sotzing, *Polym. Preprints*, **39**(1), 173 (1998).

International Conference on the Science and Technology of Synthetic Metals, Montpellier, France, July 1998.  
"Low Gap Electrochromic Polymers Based on 3,4-Ethylenedioxythiophene (EDOT)", with D. J. Irvin, J. A. Irvin, A. Kumar, G. A. Sotzing, C. A. Thomas, and D. M. Welsh

American Chemical Society, Southeast Regional Meeting, Research Triangle Park, NC, November 1998  
"Variable Gap Conjugated Polymers as Electrochromic and Electroluminescent Materials"

Materials Research Society, 1998 Fall Meeting, Boston, MA, November 1998  
"Conjugated, Luminescent, and Redox Active Polyelectrolytes for Use in Electrostatic Self Assembly", with M. B. Ramey, P. B. Balanda, J. Baur, W.-K. Woo, and M. F. Rubner

Materials Research Society, 1999 Spring Meeting, San Francisco, CA, April 1999  
"Conjugated Polymers as Multi-Color Electrochromic and Electroluminescent Materials", with D. Irvin, M. Ramey, C. Thomas, D. Welsh, W. Woo, and M. Rubner

American Chemical Society, 218th National Meeting, New Orleans, LA, August 1999  
"Symmetrically Derivatized Poly(3,4-propylenedioxythiophene), with L. J. Kloeppner and D. M. Welsh, *Polym. Preprints*, **40**(2), 792, 1999.

American Chemical Society, 218th National Meeting, New Orleans, LA, August 1999  
"Tuning the Emission Wavelength of a Series of Conjugated Polyelectrolytes", with M. B. Ramey, *Polym. Preprints*, **40**(2), 1207, 1999.



Materials Research Society, 1998 Fall Meeting, Boston, MA, November 1998  
"Light Emitting Diodes Based on CdSe Nanocrystals/Poly(p-Phenylene) Heterostructures", with  
W. K. Woo, M. G. Bawendi, J. Pinto, M. F. Rubner, M. Ramey.

### **Interactions**

Jeff Baur, Wing-Keung Woo, Erika Abbas, and Michael F. Rubner, Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA 02319

Yang Yang, UCLA, Department of Materials Science and Engineering, Los Angeles, CA

### **Transitions**

- a. Reynolds/Florida, b. Multi-Color Carbazole Based Electrochromic Polymers, c. AG Bayer, Krefeld, Germany (Dr. Bert Groenendaal), d. Bayer researchers have investigated the electrochromic and in-situ conductivity properties of some of our functionalized BEDOT-Cz based polymers.
- b. Reynolds/Florida, b. Conducting hyperbranched and dendrimer polymers, c. EIC Laboratories (Drs. David Rauh and Fei Wang) d. "Processible Conductive Resin for High Temperature Applications" F33615-97-C-5090. The UF group supplies synthetic and electrochemical expertise to EIC. A full spectroscopic and colorimetric analysis of conducting star polymers prepared at EIC was accomplished this last year.
- c. Reynolds/Florida, b. Conductive cladding materials using redox doped conducting polymers with controlled electrical and optical properties, c. Gemfire Inc. (Dr. Hilary Lackritz) d. Advanced Displays. A set of PANI and PEDOT blends in amorphous and crystalline hosts has been investigated as potential electrode materials.
- d. Reynolds/Florida, c. Light emitting polyelectrolytes for ink-jet printed LEDs, c. UCLA (Prof. Yang ), d. Advanced displays. Water soluble polyelectrolytes developed within this program were used at UCLA as light emitting and buffer materials in LEDs deposited using ink jet printing methods.
- e. Multi-Color Carbazole Based Electrochromic Polymers, AG Bayer, Krefeld, Germany (Dr. Bert Groenendaal), Bayer has synthesized and tested our alkyl-substituted BEDOT-Cz polymers in electrochromic devices (reported in Progress Report #2).

### **Inventions and Patent Disclosures**

none

## **Honors and Awards**

University of Florida, Research Foundation Professorship to John Reynolds, 1999-2001